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Terrestrial organic carbon contributions to sediments on the Washington margin

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Abstract—Elemental and stable carbon isotopic compositions and biomarker concentrations were determined in sediments from the Columbia River basin and the Washington margin in order to evaluate geochemical approaches for quantifying terrestrial organic matter in marine sediments. The biomarkers include: an homologous series of long-chain *n*-alkanes derived from the surface waxes of higher plants; phenolic and hydroxyalkanoic compounds produced by CuO oxidation of two major vascular plant biopolymers, lignin and cutin. All marine sediments, including samples collected from the most remote sites in Cascadia Basin, showed organic geochemical evidence for the presence of terrestrial organic carbon. Using endmember values for the various biomarkers determined empirically by two independent means, we estimate that the terrestrial contribution to the Washington margin is ~60% for shelf sediments, ~30% for slope sediments, and decreases further to ≤15% in basin sediments. Results from the same geochemical measurements made with depth in gravity core 6705-7 from Cascadia Seachannel suggest that our approach to assess terrestrial organic carbon contributions to contemporary deposits on the Washington margin can be applied to the study of sediments depositing in this region since the last glacial period.

INTRODUCTION

CONTINENTAL MARGINS ARE recognized as the dominant reservoir for organic carbon burial in the marine environment, receiving on a global basis an estimated 130×10^{12} g of *total* organic carbon per year (BERNER, 1982; ROMANKEVICH, 1984; WALSH, 1988). Total organic carbon (TOC) is comprised of material derived from both marine and terrestrial sources. MEYBECK (1982) estimated that the particulate discharge of terrestrial organic carbon to the world's ocean via rivers is 180×10^{12} g/y. Unless the bulk of this material is labile and degraded soon after introduction (ITTEKKOT, 1988), a problem with the global mass balance exists since the particulate input of terrestrial organic carbon exceeds by a significant factor the burial rate of total (terrestrial + marine) organic carbon in all ocean sediments (BERNER, 1982).

An accurate inventory for terrestrial and marine organic carbon in ocean sediments is essential to the quantitative understanding of biogeochemical cycles. A variety of geochemical approaches have been employed to define the marine to terrestrial blend of organic carbon buried in sediments from various regions of the ocean. Previous interpretation of isotopic ($\delta^{13}C$; GEARING et al., 1977) and lignin biomarker (HEDGES and PARKER, 1976; HEDGES and MANN, 1979b) data discounted the possibility of significant terrestrial contributions to TOC in sediments depositing seaward of shelf environments. However, the importance of terrestrial contributions to TOC buried in sediments along continental margins and even in the deep-sea may have been underestimated significantly based on more recent work with molecular biomarkers (PRAHL and MUEHLHAUSEN, 1989; GOUGH et al., 1993; JASPER and GAGOSIAN, 1993, and references therein). This change of perspective reflects the difficulty of assigning values to the endmembers required to interpret quantitative organic geochemical data. Endmember values appropriate for one region are not necessarily applicable universally and must be assigned empirically through regional study.

In this paper, we present elemental (C and N), stable isotopic ($\delta^{13}C$), and terrestrial biomarker data for organic matter in a collection of sediments from the Columbia River basin and the Washington margin. These organic geochemical data are used to evaluate different tracers and approaches for determining the terrestrial contribution to TOC in marine sediments from an environment receiving a dominant riverine input. A feature unique to our data set is that river sediments have been analyzed to determine the organic geochemical composition of source material before it is mixed with marine organic material. With these data, we evaluate some of the assumptions made in using property-property plots to predict endmember compositions and demonstrate that, in general, a multiple tracer approach is required to minimize the bias that could result if only data for a single biomarker were considered.

All of our data fit the scenario that the terrestrial component of TOC decreases with distance offshore from being the dominant fraction in shelf sediments to a minor, but nonetheless quantitatively significant fraction in slope and basin sediments. The terrestrial component in slope and basin sediments is more biodegraded than that found in shelf sediments and, in fact, looks most like bulk river sediments. Thus, specific compositional relationships determined for sediments from the shelf environment (HEDGES and MANN, 1979b) are not applicable to sediments deposited farther offshore. The larger inventory of terrestrial organic carbon now apparent in fine-grained, TOC-rich sediments from the Washington slope may be indicative of an ocean-wide phenomenon and consequently have important implications for modelling the global carbon cycle (e.g., GOUGH et al., 1993).

EXPERIMENTAL

Sample Collection

Fourteen surface sediments were collected in 1979 using a 0.025 m^2 van Veen grab sampler at midchannel sites behind the major dams located throughout the Columbia River basin (Fig. 1). The physical characteristics of these samples have been discussed elsewhere (HEDGES et al., 1984). Two additional river sediments (Mott Island: BC1 & 2 and BC5) were collected by box coring in 1989 at sites behind Tongue Point near the head of the Columbia River estuary (Fig. 1). Box cores (20 × 30 cm^2) and multiple cores (~30 cm^2) were collected at locations throughout the Washington margin (see cross-hatched area and inset, Fig. 1) on various cruises from 1975 to 1985 aboard RV *Thompson* and RV *Wecoma*. Sediment from the grabs and box cores (0–2 cm depth) were immediately subsampled and stored frozen in glass jars until chemical analysis. Whole multiple cores were frozen immediately upon collection, and later thawed, subsampled, and analyzed. The location and water column depth for each marine sampling site are given in Table 1. A set of sediment samples was also obtained from seven depths in gravity core 6705-7 collected in 1967 from Cascadia Seachannel on the Astoria Fan (2688 m water depth, 46°03.6'N 126°37.9'W). Prior to subsampling, this core had been stored since collection at 4°C in a sealed D-tube in the Oregon State University core repository.

Size Fractionation Method

Samples of river sediment from Wells Dam and Mott Island (BC1 & 2 and BC5) and a forest soil from the Willamette Valley were separated into various size fractions for chemical analysis. Size fractions > 64 μm were obtained by wet sieving bulk samples (10–20 g dry) through nested, stainless steel sieves. For the Wells Dam sediment, particles < 64 μm passing through the sieves with the wash water (~ 1 L, Milli-Q) were recovered by centrifugation. Prior to centrifugation, the wash water contained in an Erlenmeyer flask was acidified (pH ~ 2) by dropwise addition of concentrated HCl. This treatment promoted flocculation of clays (< 5 μm) and facilitated complete recovery of solids. For the Mott Island sediments, the flask containing the wash water was swirled gently and decanted immediately. Particles recovered by acidification of the decanted water and subsequent centrifugation were defined as "< 64 clay"; particles recovered from the bottom of the flask were defined as "< 64 silt." Wet size fractions isolated by this scheme were used immediately for chemical analysis.

Chemical Analyses

The methodology for hydrocarbon extraction and *n*-alkane analysis by capillary gas chromatography (GC) are provided elsewhere (PRAHL and PINTO, 1987). The precision of replicate compound measurements was ±10–15%.

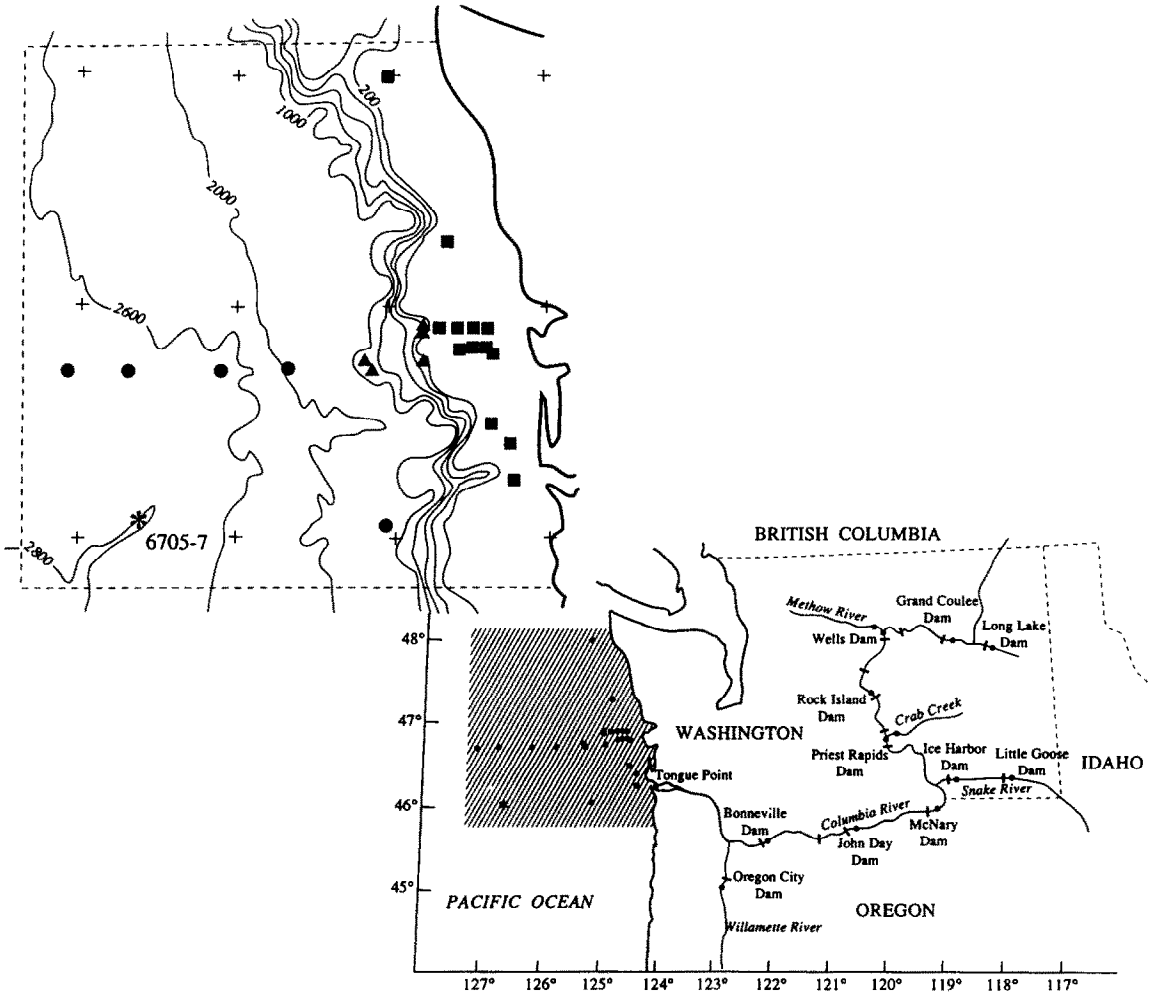

FIG. 1. Map identifies fourteen sampling locations behind major dam sites within the Columbia River drainage basin. The cross-hatched area and corresponding inset indicates twenty-three offshore sites on the Washington margin also examined in this study. The specific coordinates of shelf (filled squares), slope (filled triangles), and Cascadia Basin (filled circles) sampling locations are given in Table 1. The location for gravity core 6705-7 collected from the Cascadia Seachannel on the Astoria Fan (2688 m water depth; 46°03.6'N 126°37.9'W) is identified by the asterisk.

TABLE 1. Organic geochemical data for surface sediments on the Washington Margin.

LOCATION	DEPTH m	TOC %	C/N_a	$\delta^{13}C$ ‰	$\Sigma C_{25\text{-}31}$ µg/gC	CPI	LIG mg/gC	S/V	C/V	Va/Vh	Vo/Vh	diC_{16} mg/gC	DHA mg/gC
Continental Shelf													
46 50.1 N 124 27.0 W	55	1.0	14.7				36.6	0.27	0.05	0.28	0.25		0.73
46 55.1 N 124 25.2 W	63	0.2	16.2		160	5.0	17.5	0.23	0.04	0.27	0.28		0.14
46 25.0 N 124 18.0 W	72	0.8	13.9	-23.9			24.4	0.26	0.06	0.28	0.25		0.73
46 49.7 N 124 26.0 W	73	1.1	13.8	-22.6	155	5.4	36.7	0.21	0.04	0.37	0.29	0.66	1.76
46 14.9 N 124 14.4 W	75	0.6	17.5		160	5	26.4	0.26	0.05	0.40	0.33		0.48
46 55.1 N 124 30.5 W	87	1.3	16.9		160	5.9	37.4	0.22	0.04	0.25	0.26		0.49
46 50.0 N 124 30.0 W	90	1.1	13.9	-24.1			47.7	0.33	0.07	0.41	0.34		1.24
46 30.0 N 124 23.0 W	90	1.2	15.9	-25.5	240	4.9	84.7	0.25	0.04	0.30	0.26	0.68	2.54
47 18.1 N 124 40.3 W	104	1.0	13.1	-23.7			24.5	0.26	0.06	0.30	0.26		1.57
46 55.1 N 124 36.9 W	105	1.7	14.8		210	6.3	34.9	0.28	0.05	0.25	0.26		0.45
46 50.0 N 124 35.5 W	110	1.4	13.0		101	5.1	45.0	0.34	0.10	0.31	0.27	1.98	1.17
47 59.8 N 125 06.0 W	134	1.6	12.8	-23.3			24.9	0.27	0.06	0.31	0.32		0.50
46 55.1 N 124 44.3 W	136	1.5	12.1		130	5.1	16.3	0.24	0.05	0.28	0.27		0.31
mean		1.1	14.5	-23.9	165	5.4	35.2	0.26	0.05	0.31	0.28	1.11	0.93
std dev		0.4	1.6	0.9	41	0.5	17.1	0.04	0.02	0.05	0.03	0.62	0.67
%std dev		36	11	4	25	9	49	14	29	16	11	56	71
Continental Slope													
46 55.1 N 124 49.6 W	387	2.4	11.6		130	4.2	12.4	0.25	0.06	0.31	0.29		0.47
46 53.0 N 124 59.6 W	538	2.8	10.3		90	4.7	10.7	0.32	0.11	0.32	0.31		0.39
46 44.8 N 125 00.7 W	700	2.8	9.8	-22.0	54	3.0	7.5	0.37	0.11	0.60	0.35	0.76	1.24
46 45.6 N 125 12.0 W	980	2.0	10.5	-21.6			2.4	0.25	0.17	0.38	0.34	0.54	0.24
46 42.0 N 125 10.3 W	1004	3.5	10.5				0.32	0.32	0.15	0.57	0.37		0.42
mean		2.7	10.5	-21.8	91	4.0	7.5	0.30	0.12	0.44	0.33	0.65	0.55
std dev		0.5	0.6	0.2	31	0.7	3.7	0.05	0.04	0.12	0.03	0.11	0.35
%std dev		19	6	1	34	18	49	15	32	29	9	17	64
Cascadia Basin													
46 44.4 N 125 42.5 W	1885	2.2	9.7	-21.5			2.0	0.39	0.20	0.52	0.39	0.94	0.24
46 04.0 N 125 05.0 W	2235	1.9	9.4		52	4.3	7.6	0.43	0.29	0.45	0.38	1.90	0.75
46 44.4 N 126 09.5 W	2562	1.6	9.3	-21.5			2.1	0.34	0.23	0.66	0.50	0.45	0.21
46 43.9 N 126 42.4 W	2600	1.2	8.4	-21.5			0.7	0.43	0.35	0.71	0.38	0.55	0.18
46 44.2 N 127 07.0 W	2617	1.4	9.1	-21.2			0.5	0.69	0.03	0.69	0.41	0.41	0.13
mean		1.7	9.2	-21.4	52	4.3	2.6	0.46	0.22	0.61	0.41	0.85	0.30
std dev		0.4	0.4	0.1			2.6	0.12	0.11	0.10	0.05	0.56	0.23
%std dev		21	5	1			100	27	49	17	11	65	75

LEGEND: **TOC**, total organic carbon content in weight percent; **C/N_a**, atomic ratio for total organic carbon to total nitrogen; $\delta^{13}C$, stable carbon isotope composition of TOC; **$\Sigma C_{25\text{-}31}$**, combined C_{25}, C_{27}, C_{29}, C_{31} n-alkane concentration; **CPI**, carbon preference index calculated for $C_{20\text{-}32}$ n-alkane series; **LIG**: combined concentration of eight characteristic lignin phenols produced by CuO oxidation; **S/V**, relative concentration of total syringyl to vanillyl phenols; **C/V**, relative concentration of total cinnamyl to vanillyl phenols; **Va/Vh**, relative concentration of vanillic acid to vanillin; **Vo/Vh**, relative concentration of vanillone to vanillin; **diC_{16}**, concentration of the cutin acid x,ω-dihydroxyhexadecanoic acid; **DHA**, concentration of 3,5-dihydroxybenzoic acid.

Lignin phenols were analyzed in three different laboratories using slight modifications of an established CuO oxidation technique (HEDGES and ERTEL, 1982). Due to low lignin levels in several offshore samples, lignin phenol concentration is expressed as LIG (total mg of eight characteristic lignin phenols per g of total organic carbon). LIG corresponds to $10 \times \Lambda$, where Λ is the nomenclature defined originally by HEDGES and MANN (1979b) to express lignin phenol concentration. x,ω-Dihydroxyhexadecanoic acid (diC_{16}, where x is 8, 9 or 10) and 3,5-dihydroxybenzoic acid (DHA) were also detected and formally identified by GC/MS as major CuO oxidation products of sediments from this environment. diC_{16} is the dominant CuO oxidation product of the vascular plant biopolymer cutin, although other C_{16} and C_{18} components are also produced in significant amounts in some cases (GONI and HEDGES, 1990). diC_{16} concentration was quantified as a relative measure of sedimentary cutin content. diC_{16} data are not reported for all Washington shelf and slope sediments because several of these samples were studied well before GC conditions employed in the CuO oxidation technique were optimized for cutin acid analysis. DHA is a common CuO oxidation product of sediments and soils but not of fresh vascular plant tissues (UGOLINI et al., 1981). Typical precision for determinations of LIG, diC_{16} and the lignin phenol compositional properties (S/V, C/V, Va/Vh, Vo/Vh) were ±10%.

Total organic carbon (TOC) and nitrogen were analyzed by high temperature combustion using a Carlo Erba Elemental Analyzer after samples were pretreated chemically to remove calcium carbonate. In earliest analyses, calcium carbonate was removed by exposing samples overnight at room temperature to mineral acid (1 N HCl), then filtering and washing with distilled water. No precautions were taken by this method to prevent organic matter loss to solution. Later, a modified chemical approach was adopted for calcium carbonate removal that eliminated all question of such loss (HEDGES and STERN, 1984). Comparison of results obtained on randomly selected samples analyzed by both methods showed good agreement. Thus, none of the reported TOC are considered underestimates. The precision of TOC and atomic C/N measurements by both approaches was ±5%.

Stable isotopic composition ($\delta^{13}C$) of TOC in sediments was determined by ratio mass spectrometry. The gaseous analyte CO_2 was produced under vacuum by high-temperature CuO oxidation of powdered samples pretreated with dilute mineral acid to remove inorganic carbon (HAYES, 1983). $\delta^{13}C$ results were obtained from three different isotope facilities: soils and recent sediments were analyzed either in the College of Oceanography (Oregon State University) or at the Center for Applied Isotopic Studies (University of Georgia); samples from gravity core 6705-7 were analyzed at Coastal Science Laboratories (Austin, TX). $\delta^{13}C$, reported in permil (‰) relative to the PDB carbonate standard, are precise at least to ±0.2‰.

RESULTS

River Sediments

The total organic carbon (TOC) content of the fourteen river sediments analyzed in this study (Fig. 1) span a range from 0.2 to 3% by weight, reflecting the wide variety of sed-

TABLE 2. Organic geochemical data for sediments collected throughout the Columbia River basin.

SAMPLE	TOC %	C/N_a	$\delta^{13}C$ ‰	ΣC_{25-31} μg/gC	CPI	LIG mg/gC	S/V	C/V	Va/Vh	Vo/Vh	diC_{16} mg/gC	DHA mg/gC
Long Lake	2.8	14.4	-26.1	290	3.7	9.7	0.43	0.19	0.61	0.40	0.53	1.44
Grand Coulee	1.3	14.5	-25.2	220	4.5	13.8	0.35	0.15	0.46	0.36	0.51	1.32
Methow River	1.4	20.3		480	17.4	82.8	0.27	0.25	0.49	0.08	5.84	2.39
Wells Dam	0.5	10.9	-24.9	307	10.4	44.9	0.33	0.07	0.29	0.27	1.71	1.98
Rock Island	3.0	15.4		280	8.3	32.3	0.28	0.09	0.31	0.27	3.65	1.13
Crab Creek	2.0	11.9		290	8.0	41.3	0.92	0.56	0.39	0.28	2.02	0.91
Priests Rapid	0.9	20.5	-25.6	220	7.3	36.5	0.38	0.10	0.31	0.30	1.50	1.57
Little Goose	2.0	14.4	-25.9	250	7.1	23.1	0.34	0.11	0.37	0.31	1.34	1.39
Ice Harbor	2.1	16.0		220	4.0	16.3	0.48	0.14	0.41	0.34	0.68	1.19
McNary	1.3	12.3	-26.3	270	7.4	27.3	0.38	0.10	0.32	0.29	1.12	2.16
John Day	1.8	10.4		270	6.0	14.4	0.54	0.17	0.45	0.36	0.79	1.15
Bonneville	0.2	11.7		250	7.5	22.4	0.48	0.11	0.41	0.33	0.92	1.08
Willamette	0.3	19.1	-26.1	280	3.0	41.2	0.22	0.05	0.26	0.26	1.61	1.11
Tongue Point	0.3	15.2		130	3.3	38.8	0.22	0.06	0.29	0.27	1.05	0.89
mean	1.4	14.8	-25.7	268	7.0	31.8	0.40	0.15	0.38	0.29	1.66	1.41
std dev	0.9	3.2	0.5	73	3.6	18.1	0.17	0.12	0.09	0.07	1.39	0.45
%std dev	62	22	2	27	51	57	43	81	24	24	84	32

iment textures, coarse sand to fine-grained mud (Table 2). Atomic C/N ratios (C/N_a) range from 10.4 to 20.5 with a mean of 14.8 ± 3.2. $\delta^{13}C$ values are much more homogeneous, averaging −25.7 ± 0.5‰. TOC, C/N_a, and $\delta^{13}C$ values differ somewhat from those reported previously (HEDGES et al., 1984) for samples collected at the same time but stored and analyzed separately. The difference ranged for TOC from −0.4 to 1.3 wt%, averaging 0.0 ± 0.4 wt% (n = 14), for C/N_a from −3.1 to 7.2, averaging −0.62 ± 2.9 (n = 14) and for $\delta^{13}C$ from −3.4 to 0.4‰, averaging −0.76 ± 1.6‰ (n = 5).

An homologous series of odd-carbon predominant, long-chain n-alkanes is the major component of hydrocarbon fractions isolated from Columbia River sediments (PRAHL, 1985). The series is dominated in all cases by the four components nC_{25}, nC_{27}, nC_{29}, and nC_{31}, with nC_{29} always most abundant. The carbon preference index (CPI_{20-32}; BRAY and EVANS, 1961) measured on the series ranges from 3.0 to 17.4, averaging 7.0 ± 3.6 (Table 2). Surface waxes of higher plants are a recognized source of such series (KOLATTUKUDY, 1976). The combined concentration of the four dominant n-alkanes (ΣC_{25-31}) normalized to organic carbon is quite uniform in the sample set, averaging 268 ± 73 μg/gC.

CuO oxidation products of the vascular plant biopolymers lignin (HEDGES and MANN, 1979a) and cutin (GONI and HEDGES, 1990) were also detected in all river sediments. Total lignin phenol concentration (LIG) averages 31.8 ± 18.1 mg/gC. The compositional parameters, S/V (0.40 ± 0.17) and C/V (0.15 ± 0.12), indicate that significant amounts of lignin ultimately derived from woody and nonwoody angiosperm tissues are present (HEDGES and MANN, 1979a). Values of the ratio for vanillic acid to vanillin (Va/Vh), an indicator of aerobic biodegradation of the lignin polymer (HEDGES et al., 1988), are elevated (0.38 ± 0.09) over those measured in fresh plant material (0.15 ± 0.05; HEDGES et al., 1982). diC_{16} concentration averages 1.66 ± 1.39 mg/gC, which is near the low end of the broad range observed for this compound released by CuO oxidation of various fresh vascular plant tissues (0.8–64 mg/gC; GONI and HEDGES, 1990). DHA is present in all river sediments (1.41 ± 0.45 mg/gC).

Size-Fractionated Sediments

Table 3 presents organic geochemical data for size-fractionated river sediments and forest soil. The TOC content of the coarsest size fraction isolated from each river sediment is noticeably higher than that measured in any of the finer size fractions. The organic matter associated with coarse particles also display highest C/N_a. C/N_a of the organic matter in the coarsest size fraction quite significantly exceeds values measured in soils. In comparison, the finer size fractions display, in the case of all sediment samples, C/N_a similar to or lower than that measured in soils. The $\delta^{13}C$ of organic matter in river sediment shows no dependence on grain size (−26.0 ± 0.6‰) and is essentially identical to values measured in soils (−26.1‰).

High CPI_{20-32} identifies vascular plantwax as the dominant contributor to the long-chain n-alkane distribution in all size fractions of river sediment. Although plantwax n-alkane concentration normalized to organic carbon is not constant in the different size fractions, it shows no bias toward coarse or fine particles. In contrast, total lignin phenol concentration is consistently higher in coarse relative to fine sediment size fractions. The decline in LIG with decreasing particle size is accompanied by an increase in values of Va/Vh. The grain size dependence of diC_{16} concentration is less clear than for lignin phenols. But, diC_{16} concentrations appear to decrease in the finer size fractions as well. DHA is found throughout the particle size range and is particularly abundant in soil samples.

Marine Sediments

Table 1 displays organic geochemical data for sediments from the Washington margin grouped according to different depositional environments. TOC is lowest on the shelf (1.1 ± 0.4% by weight), increases to a maximum in slope sediments (2.7 ± 0.5%) and declines farther offshore in Cascadia Basin (1.7 ± 0.4%). C/N_a decreases progressively from shelf (14.5 ± 1.6) to slope (10.5 ± 0.6) to basin (9.2 ± 0.4) sediments

TABLE 3. Organic geochemical data for size fractionated sediments from the Columbia River and soil from the Willamette Valley.

	TOC %	C/N_a	$\delta^{13}C$ ‰	ΣC_{25-31} μg/gC	CPI	LIG mg/gC	S/V	C/V	Va/Vh	Vo/Vh	diC_{16} mg/gC	DHA mg/gC
Sediment Samples												
Wells Dam[@]												
>500	29.5	33.5	-26.6	373	13.0	145	0.27	0.05	0.27	0.21		2.32
250-500	0.5	11.3	-25.3	211	10.8	43	0.35	0.05	0.30	0.24		1.51
125-250	0.2	6.4	-25.3	161	9.0	49	0.36	0.07	0.33	0.26		2.50
64-125	0.3	8.0	-25.4	280	7.1	51	0.43	0.08	0.34	0.43		2.45
<64	0.7	10.6	-25.6	416	8.4	21	0.37	0.11	0.40	0.37		1.72
Mott Island BC1&2												
>250	9.5	14.9				77	0.46	0.14	0.25	0.24	2.62	1.46
64-250	1.8	10.2				78	0.39	0.11	0.27	0.24	3.51	1.64
<64 silt	0.6	9.5				37	0.37	0.11	0.32	0.28		1.44
<64 clay	2.9	8.8				34	0.38	0.11	0.39	0.30	2.28	1.53
Mott Island BC5												
>250	7.0	19.8	-26.1			79	0.42	0.11	0.24	0.23	2.53	1.19
64-250	2.0	12.5	-26.4			72	0.37	0.08	0.27	0.25	3.24	1.80
<64 silt	0.8	11.5	-26.7			35	0.35	0.10	0.34	0.28	1.96	1.51
<64 clay	1.9	8.7	-26.2			35	0.32	0.10	0.34	0.28	1.47	1.44
Soil samples												
Coniferous forest	1.6	13.7	-26.0	71	5.2	146	0.22	0.18	0.54	0.39	26.28	17.67
Deciduous forest												
>250	3.3	13.4		65	6.9	36	0.72	0.17	0.41	0.30	0.61	1.99
64-250	2.1	12.5		132	7.9	36	0.40	0.08	0.45	0.31	4.59	2.58
<64	1.8	11.1	-26.2	100	8.4	30	0.30	0.07	0.59	0.36	0.69	2.89

[@]all data for this sample from Pinto (1988)

while $\delta^{13}C$ becomes progressively heavier along this sampling trajectory (−23.9, −21.8, and −21.4‰, respectively).

All sediments from the Washington margin contain a terrestrial *n*-alkane distribution indicative of riverine input (PRAHL, 1985; PRAHL et al., 1992). ΣC_{25-31} in the shelf sediments (165 ± 41 μg/gC) average ~⅔ that of river sediments and decrease offshore by a factor of 3. CPI_{20-32} measured on *n*-alkane series in all surface marine sediments fall between 3 and 6.3, within the range observed for river sediments.

The presence of lignin-derived phenols was confirmed unambiguously by GC/MS in all sediments from the Washington margin, including those deposited most remotely in Cascadia Basin. LIG averages 35.2 ± 17.1 mg/gC in shelf sediments, a value consistent with results from previous work in this region (HEDGES and MANN, 1979b) and comparable to the average for bulk river sediments (31.8 ± 18.1). LIG decreases offshore to values as low as 0.5 mg/gC in sediments from Cascadia Basin. Values for the lignin phenol compositional parameters S/V, C/V, and Va/Vh are lower in shelf sediments than river sediments, suggesting shelf sediments contain fresher plant debris enriched in woody material than the river sediments. All of these ratios increase progressively offshore to values typically higher than observed in river sediments.

Like plantwax *n*-alkanes, diC_{16} and DHA concentrations decrease in the sequence from river to deep water sediments. In addition, we have observed that values for the ratio of 3,5-dihydroxybenzoic acid to total vanillyl phenols (DHA/V) increase in direct proportion with Va/Vh ratios and with increasing distance offshore (Fig. 2). The x-intercept of the line fitted by least squares analysis to the river data equals 0.19, which lies within the range of Va/Vh typical of fresh vascular plant tissues (0.15 ± 0.05; HEDGES et al., 1982). Based on these results, we propose that DHA is a product of soil processes and that it can be used to trace soil organic matter. This view is potentially equivocal, however, since recent work has shown kelps and other brown macroalgae produce significant yields of DHA upon CuO oxidation (GONI, 1992).

Cascadia Seachannel Core

Sediment samples from seven depths in a gravity core (6705-7) from Cascadia Seachannel on the Astoria Fan (Fig. 1) were analyzed for TOC content, $\delta^{13}C$, and C/N_a compo-

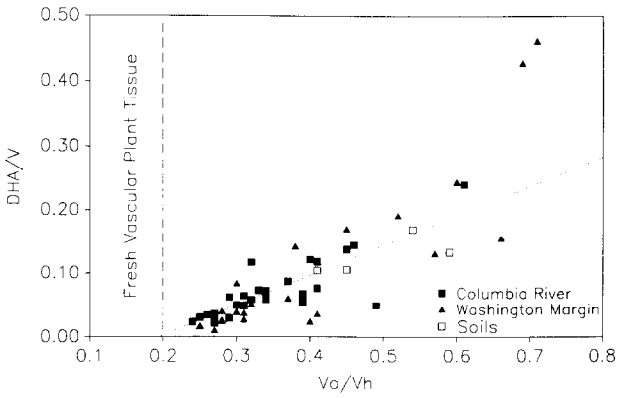

FIG. 2. Scatter plot of values for the ratio of 3,5-dihydroxybenzoic acid to total vanillyl phenols (DHA/V) vs. the ratio of vanillic acid to vanillin (Va/Vh) measured in bulk (Table 2) and size-fractionated (Table 3) sediments from the Columbia River basin and in surface sediments from the Washington margin (Table 1). The solid line depicts the least squares regression of all river data (DHA = 0.469 × Va/Vh − 0.091, $r^2 = 0.69$). Data for forest soils from the Willamette valley are also plotted for comparison.

TABLE 4. Organic geochemical data for gravity core 6705-7 from Cascadia Seachannel.

DEPTH cm	TOC %	C/N_a	$\delta^{13}C$ ‰	ΣC_{25-31} μg/gC	CPI	LIG mg/gC	S/V	C/V	Va/Vh	Vo/Vh	diC_{16} mg/gC	DHA mg/gC
24	1.14	10.0	-22.6	56	2.7	5.5	0.35	0.13	0.74	0.46	0.45	1.08
45	1.10	10.5	-22.6	82	3.1	6.9	0.38	0.12	0.73	0.44	0.37	1.17
127	1.01	11.6	-23.2	133	4.6	13.0	0.47	0.09	0.67	0.42	0.40	1.94
170	0.73	12.3	-23.2	185	4.7	14.5	0.35	0.09	0.50	0.33	0.35	1.54
212	0.51	11.7	-23.1	181	4.1	6.9	0.31	0.12	0.72	0.43	0.32	1.11
286	0.38	11.2	-23.8	225	3.6	7.6	0.35	0.11	0.87	0.45	0.35	1.26
364	0.50	11.3	-24.1	188	3.3	10.2	0.36	0.14	0.58	0.39	0.41	1.60
mean	0.77	11.2	-23.2	150	3.7	9.2	0.37	0.11	0.69	0.40	0.38	1.39
std dev	0.29	0.8	0.5	57	0.7	3.2	0.05	0.02	0.11	0.04	0.04	0.29
%std dev	38	6	2	38	19	34	13	15	16	10	10	17

sition and concentrations of plantwax *n*-alkanes (ΣC_{25-31}) and CuO oxidation products of lignin (LIG) and cutin (diC_{16}) (Table 4). TOC decreases steadily with depth by a factor of ≥2 over the 3.6 m interval of core examined. The decline in TOC is accompanied by a shift with depth to more negative $\delta^{13}C$ and higher C/N_a. Hydrocarbon fractions isolated from all intervals are dominated by a C_{20-32} series of *n*-alkanes characteristic of higher plantwax origin. ΣC_{25-31} normalized to organic carbon increases with depth by a factor of 3 from a near-surface value typical of recent sediments depositing throughout this region of the Washington margin (Table 1). LIG varies two- to threefold in these samples but shows no systematic trend with depth. In contrast, diC_{16} concentration is constant with depth.

DISCUSSION

The Columbia River is the primary source of terrestrial organic carbon in sediments depositing on the Washington margin (LANDRY and HICKEY, 1989). Previous organic geochemical analyses using stable carbon isotopes and lignin phenols (HEDGES and MANN, 1979b) suggested that shelf sediments were the main depository for riverine organic matter and that, based on projections from shelf data, little terrestrial carbon is exported to sedimentary deposits farther offshore. Our results reveal the presence of suites of terrestrial biomarkers in sediments throughout the Washington margin, including the hemipelagic region in Cascadia Basin. In order to translate biomarker abundance into terrestrial organic carbon equivalents, we will evaluate two approaches for quantifying terrestrial organic matter in mixture with marine organic matter and compare assessments derived from multiple organic geochemical tracers.

Given our sedimentary system which receives input from a single riverine source, we can use organic geochemical data for riverine material to define the composition of terrestrial biomarkers entering the marine environment and, more importantly, determine the relationship between biomarker and terrestrial organic carbon concentrations. The latter information is needed to ascertain from biomarker concentrations the blend of terrestrial and marine organic carbon in offshore sediments. The main requirement for this first approach is that representative samples of the terrestrial material exported to the ocean must be analyzed. Surface sediments collected behind major dams on the Columbia River were chosen to evaluate the riverine endmember. Although these samples may not perfectly represent the bulk sedimentary material transported down river (BEASLEY et al., 1986), they do provide a longer term compositional average of the potential riverine input to the ocean than would instantaneous snapshots of suspended sediment sampled near the river mouth.

The second approach we use to quantify terrestrial organic contribution involves determining relationships among individual terrestrial biomarker concentrations, elemental and isotopic compositions in marine sediments. We chose to investigate terrestrial biomarkers that are exclusively derived from vascular plant sources and thus have no marine origin. Terrestrial biomarker concentrations should decline proportionally to the amount of terrestrial organic matter in sediments and equal zero at sites where the sedimentary organic matter is completely marine derived. The elemental (C/N_a) and isotopic ($\delta^{13}C$) composition of organic matter also varies systematically between marine and terrestrial sources (e.g., JASPER and GAGOSIAN, 1989). However, numerous biological and environmental factors can affect the marine and terrestrial endmember composition for these bulk properties. So, values of the marine and terrestrial endmembers for these properties are always non-zero and must be determined empirically for each environment. We can estimate the marine endmembers for C/N_a and $\delta^{13}C$ by relating our terrestrial biomarker data to the elemental and isotopic compositions and projecting the relationship to zero biomarker concentration (e.g., see HEDGES and MANN, 1979b). The assignment of values for the terrestrial endmember of C/N_a and $\delta^{13}C$ by this correlation approach is much more tenuous and, to be done reliably, requires either an unambiguous marine biomarker (JASPER and GAGOSIAN, 1993) or knowledge of additional information such as the data acquired in this study for Columbia River sediments.

Both approaches we employ to assess the terrestrial organic carbon contribution to marine sediments assume a consistent relationship exists between biomarker concentration and riverine organic carbon. Notably, this assumption does not necessitate inert behavior for the biomarker and its associated organic carbon in the marine environment. Degradation can occur, but the degradative process must affect both properties proportionately so that the biomarker endmember value remains unaltered (HEDGES and PRAHL, 1993).

Approach 1: Riverine Endmembers

Organic carbon levels in the fourteen Columbia River sediments analyzed in this study varied by an order of magnitude depicting the wide range of sediment types and organic mat-

ter-particle associations represented by the samples. However, elemental and, in particular, stable carbon isotopic ratios for the sedimentary organic matter are remarkably uniform and independent of organic carbon content. Both the average C/N_a (14.8 ± 3.2) and $\delta^{13}C$ (−25.7 ± 0.5‰) composition (Table 2) closely match soil attributes (Table 3), implying that the bulk of the organic carbon in these sediments ultimately derives from land plants. This conclusion seems surprising since there are other potentially significant sources of organic carbon to these sediments, including phytoplankton production within the river. It is not clear whether terrestrial organic carbon overwhelms autochthonous sources or is more stable and selectively preserved in the sediments. Nonetheless, our data for the bulk properties of organic matter in the river sediments imply that biomarkers derived from vascular plants might be good indicators for riverine contribution to the TOC in marine sediments depositing on the Washington margin.

Although organic carbon concentrations vary tenfold in the river sediments, biomarker concentrations normalized to organic carbon are generally more consistent, especially for the plantwax *n*-alkanes (Table 2). In other words, there is a significant, positive linear relationship between terrestrial biomarker concentration (per g dry sediment) and the amount of organic carbon in the river sediments. Scatter plots for plantwax *n*-alkane, lignin phenol, and cutin acid concentration vs. TOC (Fig. 3) illustrate this feature of the data. Least squares fit of each data set for all fourteen river samples yields the following regression lines:

$$\Sigma C_{25\text{-}31} = 280 \times \text{TOC} - 0.044 \ (r^2 = 0.88)$$

$$\text{LIG} = 20.2 \times \text{TOC} + 0.117 \ (r^2 = 0.30)$$

$$\text{diC}_{16} = 2.01 \times \text{TOC} - 0.003 \ (r^2 = 0.33).$$

Examination of Fig. 3 reveals that one sample, the Methow River, falls significantly above the regression lines for the three biomarkers. The Methow River sample is a coarse sandy sediment that has extremely high C-normalized concentrations of all biomarkers (Table 2) and the highest CPI and lowest vanillone to vanillin (Vo/Vh; ERTEL and HEDGES, 1985) ratios of any sample in this study, including the size-fractionated sediments. These results indicate that this sedimentary organic matter is highly enriched in vascular plant debris and is atypical of organic matter in sediments throughout the drainage basin. Removal of the Methow River sample from the data set causes only minimal changes in the slopes and intercepts, but increases the correlation coefficients for the three regression lines to 0.97, 0.51, and 0.45, respectively.

Plantwax *n*-alkane concentration shows a remarkably linear fit with sedimentary TOC. The strong correlation and a near-zero intercept of the correlation line indicate that $\Sigma C_{25\text{-}31}$ provides a well-behaved quantitative indicator of the TOC content of surface sediment present throughout the geographically diverse Columbia River basin (HIGHSMITH, 1973).

Total lignin phenol concentrations regressed against TOC in the river sediments show significantly greater variability than plantwax *n*-alkanes, particularly at higher TOC levels. The compositional parameters, S/V and C/V, also vary significantly in these samples, indicating that the blend of vascular plant material contributing to sedimentary lignin content is not uniform on a basinwide scale (HEDGES et al., 1984). Since the CuO oxidation yield of total lignin phenols per unit of organic carbon can vary by a factor ≥ 10 in fresh plant tissues depending on which plant species are examined (HEDGES and MANN, 1979a), the degree of correlation between LIG and TOC is more surprising than the variability, however.

One explanation for the relatively low scatter in the lignin phenol content of sediments compared to plants is that the bulk of the lignin in these sediments derives not from discrete vascular plant debris but from some other, more homogenized and partially degraded source like soil humic substances. The elevated Va/Vh ratios (Table 2) indicate that some aerobic biodegradation of the lignin component has occurred. And, the relatively high abundances of DHA, which is concentrated in soil organic fractions (Table 3), suggest that this transformation could have happened in soils prior to mobilization into the river. In fact, the reasonably linear relationship between DHA/V and Va/Vh for the river and soil samples (Fig. 2) implies that DHA is a product of soil processes and might be directly linked to lignin biodegradation. LIG values measured in humic material isolated from soils and sediments (ERTEL and HEDGES, 1984) are much lower than those measured in intact plant fragments isolated from corresponding samples (ERTEL and HEDGES, 1985). Degradative processes occurring in the surrounding soils could modify and reduce the lignin and cutin component in organic matter that has the bulk compositional properties (C/N_a and $\delta^{13}C$) of vascular plant source material. As stated above, one exception to this could be the Methow River sediment, which appears to contain high levels of relatively fresh plant debris.

Cutin acid concentrations (diC_{16}) regressed against TOC in river sediments also show significantly greater variability than do plantwax *n*-alkane concentrations. The biopolymer cutin is associated with nonwoody plant tissues as are surface waxes. So, it might be expected that diC_{16} concentrations would be distributed in sediments more similarly to plantwax *n*-alkanes ($r^2 = 0.52$) than to lignin phenols ($r^2 = 0.85$), the latter being most concentrated in woody plant tissues. However, this expectation is not borne out by the data and the reason remains unclear. diC_{16} concentration in the river sediments is significantly lower than in plants. Like the case for lignin phenols, cutin acid concentrations vary by factors of 5–10 in fresh plant tissues, depending on the plant type (GONI and HEDGES, 1990), but tend to be more uniform in the sedimentary organic matter (Tables 2 and 3). Either the cutin component of these sediments derives from a few dominant plant species or diagenetic processes occurring primarily within soils have reduced the variability found in living plants. We favor the latter explanation but cannot prove our point of view with the available data.

Assuming our river samples are representative of material exported offshore, we can use the slopes of the regression lines in Fig. 3 to constrain the quantitative relationship between the biomarker concentration and terrestrial organic carbon content of marine sediments on the Washington margin. TOC in offshore deposits is a mixture of organic carbon contributed from both marine (OC_{mar}) and terrestrial (OC_{terr}) sources, i.e.,

$$\text{TOC} = OC_{mar} + OC_{terr}.$$

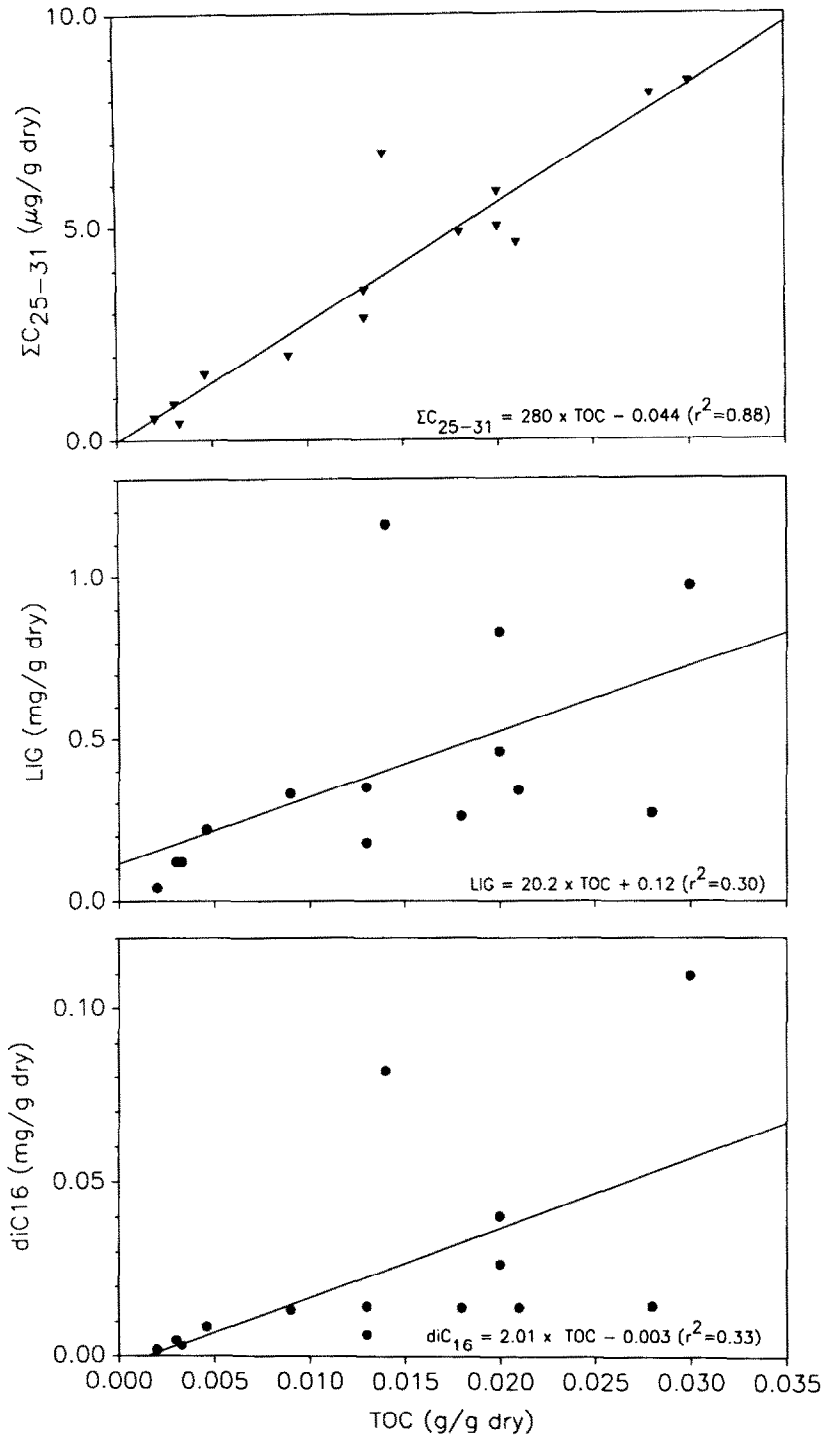

FIG. 3. Scatter plots of (a) *n*-alkane ($\Sigma C_{25\text{-}31}$, μg/g dry), (b) lignin phenol (LIG, mg/g dry), and (c) cutin acid (diC_{16}, mg/gC) concentration vs. total organic carbon (TOC, g/g dry) content in fourteen sediments collected throughout the Columbia River basin. The regression lines and coefficients of variation (r^2) obtained by least squares analysis of each data set are shown.

The percentage of terrestrial organic carbon (%TERR) in sediments on the Washington margin is estimated from the simple ratio of biomarker concentration (μg or mg/g total organic carbon) measured in a sample (Table 1) to the slope of the biomarker vs. TOC regression line for river sediments, i.e.,

$$\%\text{TERR} = (\Sigma C_{25\text{-}31}/280) \times 100$$

$$\%\text{TERR} = (\text{LIG}/20.2) \times 100$$

$$\%\text{TERR} = (diC_{16}/2.01) \times 100.$$

%TERR calculated by this means for marine sediments from the Washington margin are shown in Table 5 (see columns under Approach 1), grouped according to different depositional environments.

%TERR estimated from plantwax *n*-alkane data by this approach suggest that terrestrial contribution accounts for >50% of TOC in shelf sediments and ~20–30% of TOC in slope and basin sediments. Lignin phenol concentrations follow the same general spatial pattern of distribution in sediments on the Washington margin providing further support for an offshore decline in terrestrial contribution to TOC. However, the %TERR estimates from the lignin phenol data are much greater than 100% for the shelf sediments and, therefore, are unrealistic. %TERR estimated from the limited cutin acid data are all feasible results and indicate a significant but more uniform terrestrial contribution to TOC in sediments throughout the region than implied by either the plantwax *n*-alkane or lignin phenol data.

The lignin-derived %TERR estimates exceed 100% on the shelf because the lignin phenol content of sediments from this environment is significantly greater in all but two cases than the average value defined by least squares analysis for river sediment (Fig. 3b). Compositional data for lignin phenols (S/V, C/V, Va/Vh) on the shelf (Table 1) also differ markedly from river compositions (Table 2) and indicate that shelf sediments contain a greater proportion of lignin as discrete fragments of vascular plant debris than do river sediments or marine sediments depositing farther offshore. Up to 25% of the TOC and 53% of the lignin phenols in shelf sediments are present within vascular plant debris separable by density flotation (ERTEL and HEDGES, 1985), while little or no low density material is recoverable by this method applied to finer grained sediments depositing farther offshore (J. R. Ertel, unpubl. data). Our study of size-fractionated river sediment shows that lignin phenols, in particular, are not uniformly distributed relative to organic carbon between grain sizes (Table 3). The coarsest size fractions of sediments appear consistently more enriched in lignin phenols relative to organic carbon than finer size fractions. Hydrodynamic processes, known to operate on the Washington margin, act to trap coarse, lignin-rich woody plant debris preferentially in the shelf environment and allow other finer, lignin-poor riv-

TABLE 5. Assessment of terrestrial contribution to TOC (%TERR) in sediments from various depositional regions on the Washington margin.

LOCATION	DEPTH m	Approach 1 $\Sigma C_{25\text{-}31}$	Approach 1 LIG	Approach 1 diC_{16}	Approach 2 $\Sigma C_{25\text{-}31}$ derived $\delta^{13}C$	Approach 2 $\Sigma C_{25\text{-}31}$ derived C/N_a	Approach 2 LIG derived $\delta^{13}C$	Approach 2 LIG derived C/N_a
Continental Shelf								
46 50.1 N 124 27.0 W	55		181			99		98
46 55.1 N 124 25.2 W	63	57	87			121		122
46 25.0 N 124 18.0 W	72		121		68	87	58	86
46 49.7 N 124 26.0 W	73	55	182	33	45	85	28	84
46 14.9 N 124 14.4 W	75	57	131			140		143
46 55.1 N 124 30.5 W	87	57	185			131		133
46 50.0 N 124 30.0 W	90		236		71	87	63	86
46 30.0 N 124 23.0 W	90	86	419	34	96	116	95	117
47 18.1 N 124 40.3 W	104		121		64	75	53	73
46 55.1 N 124 36.9 W	105	75	173			100		100
46 50.0 N 124 35.5 W	110	36	223	99		73		71
47 59.8 N 125 06.0 W	134		123		57	70	44	68
46 55.1 N 124 44.3 W	136	46	81			60		57
mean		59	174	55	67	96	57	95
Continental Slope								
46 55.1 N 124 49.6 W	387	46	61			52		49
46 53.0 N 124 59.6 W	538	32	53			33		29
46 44.8 N 125 00.7 W	700	19	37	38	34	25	14	21
46 45.6 N 125 12.0 W	980		12	27	27	36	5	32
46 42.0 N 125 10.3 W	1004		23			36		32
mean		33	37	32	30	36	9	32
Cascadia Basin								
46 44.4 N 125 42.5 W	1885		10	47	25	24	2	19
46 04.0 N 125 05.0 W	2235	19	38	95		19		14
46 44.4 N 126 09.5 W	2562		10	22	25	18	2	13
46 43.9 N 126 42.4 W	2600		3	28	25	5	2	-1
46 44.2 N 127 07.0 W	2617		3	21	20	14	-4	9
mean		19	13	42	24	16	1	11
Gravity Core 6705-7								
24-28 cm		20	27	22	45	28	28	24
45-46 cm		29	34	18	45	36	28	32
127-128 cm		48	64	20	55	52	42	49
170-171 cm		66	72	17	55	63	42	60
212-213 cm		65	34	16	54	54	40	51
286-287 cm		80	38	17	66	46	56	43
364-365 cm		67	50	20	71	48	63	45
Assigned Endmembers								
Marine		0	0	0	-20.1	8.11	-21.4	8.49
Terrestrial		280	20.2	2.01	-25.7	14.8	-25.7	14.8

erine particles to advect farther offshore (PRAHL, 1985; KEIL et al., 1994). Consequently, it seems inappropriate to quantify terrestrial organic carbon contributions in all marine sediments using a universal value for the lignin phenol endmember as we have done in this approach. However, our first approach appears to work well for the plantwax *n*-alkanes, because they are more evenly distributed among the different particle size fractions of the sediments (Table 3).

Approach 2: Biomarker Relationships in Marine Sediments

All marine sediments examined in this study contain terrestrial biomarkers. Thus, some fraction of riverine organic matter is found in sediments throughout the Washington margin. Terrestrial biomarker concentrations normalized to TOC decrease offshore as expected due to dilution with marine organic matter (Table 1). C/N_a and $\delta^{13}C$ values show progressive changes with increasing water depth toward values found in marine organic matter. The linear correlation between these two bulk properties of organic carbon is strong ($r^2 = 0.88$, $n = 12$) and described by the equation, $C/N_a = -1.68 \times \delta^{13}C - 26.6$. However, since all sediments contain terrestrial biomarkers, albeit at low concentrations in several cases, we cannot unambiguously assign C/N_a or $\delta^{13}C$ values from any of these sediments as values of the marine endmember for these properties. But, we can constrain the marine endmember value for each of these properties by extrapolating correlation lines for terrestrial biomarker concentrations vs. C/N_a or $\delta^{13}C$ to zero biomarker concentration. Then, using the average river values for C/N_a and $\delta^{13}C$ for the terrestrial endmembers, we can create a mixing line to calculate %TERR from the sedimentary C/N_a and $\delta^{13}C$ values.

We have examined the correlations between terrestrial biomarkers ($\Sigma C_{25\text{-}31}$, LIG, diC_{16}) and bulk organic carbon parameters (C/N_a and $\delta^{13}C$) in our set of marine sediments (Table 1). Strongest correlations ($r^2 \geq 0.8$) are found between plantwax *n*-alkane or total lignin phenol concentration and $\delta^{13}C$ composition. Weaker correlations exist between the concentration for these two terrestrial biomarkers and C/N_a composition ($r^2 = 0.74$ and 0.58, respectively). And, virtually no correlation is evident between concentration for the single cutin acid diC_{16} and either bulk parameter ($r^2 = 0.04$ and 0.00, respectively).

Figure 4a displays a plot of plantwax *n*-alkane concentration (per gC) vs. $\delta^{13}C$ composition. The correlation line $\Sigma C_{25\text{-}31} = -45.6 \times \delta^{13}C - 915$ ($r^2 = 0.84$) fitted by least squares is defined by only three points, but passes nearly through the average value for the terrestrial endmember defined by analysis of Columbia River sediments. This observation suggests that the line could represent a binary mixing curve for riverine and marine organic carbon. The $\delta^{13}C$ composition of marine organic carbon predicted by the *x*-intercept of this line is −20.1‰, a value significantly more positive than previous estimates for the marine endmember of $\delta^{13}C$ (−21.7‰; HEDGES and MANN, 1979b) but within the range for marine organic matter (DEGENS, 1969). If the riverine endmember is included in the regression, the intercept decreases slightly (−20.2‰) with little change in the slope of the line.

Lignin phenol concentration plotted vs. $\delta^{13}C$ composition for all marine sediments fall along the same correlation line previously reported by HEDGES and MANN (1979b). Least squares fit of the combined data sets is described by the equation, $LIG = -16.8 \times \delta^{13}C - 362$ ($r^2 = 0.86$, $n = 20$). The marine endmember for $\delta^{13}C$ predicted by this equation is −21.5‰, a value virtually identical to the assessment of HEDGES and MANN (1979b). However, we have chosen to segregate data for shelf sediments from data for slope and basin sediments and plot in Fig. 4b (see dotted line) a separate correlation line for these data. This decision is based on previously discussed differences in the types of lignin found in shelf and slope sediments (Table 1) and our interpretation of Fig. 2 to show progressive enrichment of soil-derived DHA relative to recognizable lignin phenols (V) with distance offshore. Other recent investigations have indicated that the lignin source changes from relatively undegraded vascular plant debris in shelf sediments to more degraded, perhaps soil-derived organic matter farther offshore as a consequence of differential dispersal of riverine particles on the Washington margin (PRAHL, 1985; PRAHL et al., 1992; KEIL et al., 1994).

The correlation line for data from the slope and Cascadia Basin sediments is distinct ($LIG = -9.4 \times \delta^{13}C - 201$, $r^2 = 0.88$). Its slope is significantly lower than the previous but the *x*-intercept is approximately the same (−21.3‰). Notably, this line extrapolates much closer to the average terrestrial endmember value for lignin phenols determined for Columbia River sediments than the correlation line defined with shelf data included. As previously inferred from the spatial trends in data for lignin phenol composition (Tables 1 and 2), this observation indicates that sediments deposited beyond the shelf break on the Washington margin contain organic carbon like that in average Columbia River sediment intermixed with marine organic carbon. If the river-derived terrestrial endmember values for lignin phenols and $\delta^{13}C$ are included in the off-shelf data set, as seems valid in view of the plantwax *n*-alkane data (Fig. 4a), then the slope of the correlation line ($r^2 = 0.98$) declines slightly (−6.2) and the *x*-intercept shifts to a more positive value (−21.1‰).

Correlation lines for $\Sigma C_{25\text{-}31}$ and LIG vs. N/C_a are obtained by applying the same general approach (Fig. 5). The best linear fit of $\Sigma C_{25\text{-}31}$ and N/C_a data for all marine sediments (Fig. 5a) is expressed by the equation, $\Sigma C_{25\text{-}31} = -3065 \times N/C_a + 378$ ($r^2 = 0.74$, $n = 11$), which yields an *x*-intercept of 0.123 or a C/N_a ratio of 8.11. Similarly, the best linear fit of LIG and N/C_a data for just the slope and basin sediments is described by the equation $LIG = -320 \times N/C_a + 37.7$, ($r^2 = 0.58$, $n = 10$), which has an *x*-intercept of 0.118 or a C/N_a ratio of 8.49. Contrary to the pattern seen with $\delta^{13}C$, both these lines fall significantly below the range described by the river sediments. These results could indicate that C/N_a ratios in marine sediments are higher than predicted from a linear mixing line with the river sediments, possibly due to selective remineralization of the riverine nitrogen component. If this interpretation is true, then nitrogen concentrations are not conservative and cannot be used to calculate the riverine contribution to marine sediments.

With the marine endmembers established, we can use the average river values for $\delta^{13}C$ (−25.7‰) and C/N_a (14.8) as good estimates of the terrestrial endmembers for these prop-

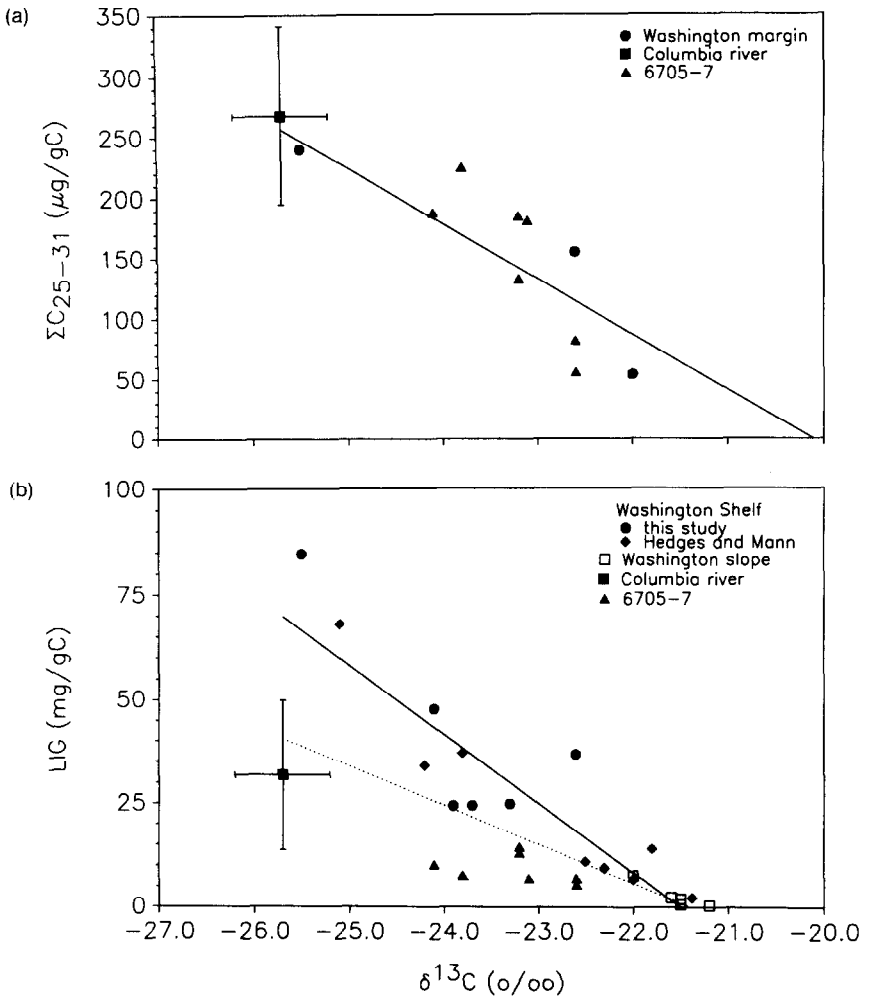

FIG. 4. Scatter plot of (a) *n*-alkane concentration (ΣC_{25-31}, μg/gC) and (b) lignin phenol concentration (LIG, mg/gC) vs. $\delta^{13}C$ composition of TOC measured in sediments from the Washington margin and at different depths in gravity core 6705-7 from Cascadia Seachannel. Average values for ΣC_{25-31} (268 ± 73 μg/g TOC), LIG (31.8 ± 18.1 mg/gC) and $\delta^{13}C$ (−25.7 ± 0.5‰) measured in sediments throughout the Columbia River basin are also plotted. Additional published data (HEDGES and MANN, 1979b) for LIG and $\delta^{13}C$ in Washington shelf sediments are included in (b) for reference. Solid lines depict the least squares regression of ΣC_{25-31} and LIG data for all marine sediments from the Washington margin including results obtained by HEDGES and MANN (1979b). The dotted line in (b) depicts the least squares regression of LIG data for only those sediments deposited seaward of the shelf. Data from 6705-7 are also plotted on each graph to show their relationship to the calibration lines established for recent sediment from the Washington margin.

erties. Thus, the terrestrial contribution to TOC (%TERR) in the various marine sediments can be calculated from elemental and isotopic data given in Table 1 ([sediment]), values for the terrestrial ([terr]) endmembers from river data and marine ([mar]) endmembers determined from regressions with each biomarker, and the following binary mixing equation:

$$\%\text{TERR} = ([\text{sediment}] - [\text{mar}])/([\text{terr}] - [\text{mar}]) \times 100.$$

Results obtained by approach 2 are also shown in Table 5. The %TERR calculated from C/N_a ratios for both biomarkers are comparable due to the similarity of the predicted marine endmembers. Although the plantwax *n*-alkanes yield a lower C/N_a marine endmember than the lignin phenols, the difference in the ranges determined by these values with the terrestrial endmember is small. As in the case for lignin phenols using approach 1, the C/N_a ratios predict %TERR for shelf sediments to be equal to or greater than 100%. These model results are unrealistic, and indicate that this method of assessment is not feasible for this environment, possibly due to selective remineralization of the nitrogen component. The %TERR calculated from $\delta^{13}C$ ratios are significantly larger for the plantwax *n*-alkanes than for lignin phenols, particularly for the sediments from the Cascadia Basin, because of the more positive marine endmember predicted by the plantwax *n*-alkanes than by the lignin phenols. However, since the regression line for plantwax *n*-alkanes contains only four points, these differences should not be overinterpreted. These calculations clearly show that the %TERR estimates are sensitive to the choice of endmember values. In spite of these differences, the results reveal a spatial pattern of distribution for terrestrial organic carbon contribution on the

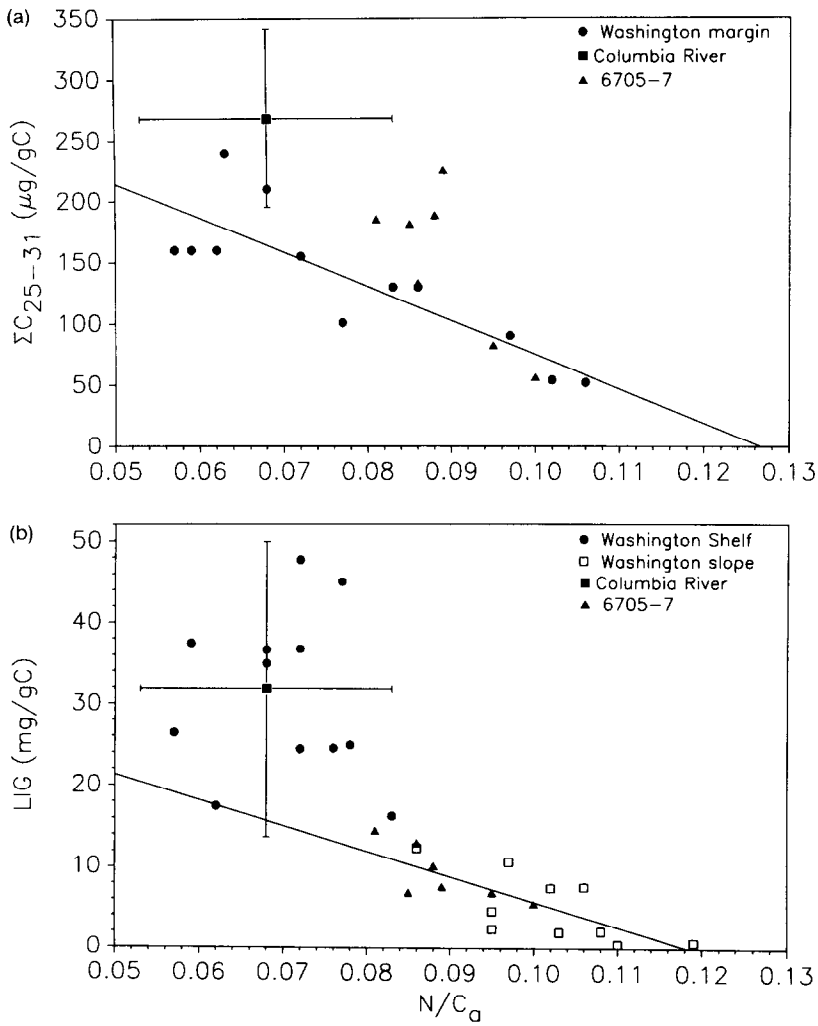

FIG. 5. Scatter plot of (a) *n*-alkane concentration (ΣC_{25-31}, μg/gC) and (b) lignin phenol concentration (LIG, mg/gC) vs. N/C_a ratios from sediments from the Washington margin and gravity core 6705-7 from Cascadia Seachannel. Mean and standard deviation of the sediments from the Columbia River (Table 2) are also included. As in Fig. 4, regression lines are derived from data for all marine surface samples in the case of ΣC_{25-31} and for only sediments deposited seaward of the shelf in the case of LIG.

Washington margin that is consistent with our assessment made by approach 1. Therefore, we conclude that terrestrial sources account for ~60% of TOC in shelf sediments, for ~30% of TOC in slope sediments grading to ≤15% of TOC in sediments from Cascadia Basin.

Paleoenvironmental Implications for the Cascadia Seachannel

Seven intervals of gravity core 6705-7 from Cascadia Seachannel spanning ~3.6 m depth were analyzed for the same set of molecular biomarker and bulk carbon compositional data (Table 4). These data were examined to evaluate whether calibrations established for these properties and used to assess terrestrial contribution to TOC in contemporary sediments from the Washington margin also apply to older sediments in this environment. The seven intervals span a time range of ~20–30 ky assuming ~13 cm/ky as an average sedimentation rate (GRIGGS, 1969).

Using the approaches described above, binary mixing analyses for all biomarkers except cutin indicate that the terrestrial component of TOC (%TERR) increases with depth in the core by 60 to 300% (Table 5). Estimates for %TERR at the top of the core range from 20–45% and increase to 50–70% by 365 cm. Systematic increases in the %TERR are seen using the $\delta^{13}C$ data, but the lignin phenol, C/N_a, and perhaps plantwax *n*-alkane data yield profiles which show mid-core maximum, albeit at different depths. The %TERR estimates based on the biomarker concentrations (approach 1) are more prone to variability than those derived from $\delta^{13}C$ (approach 2), since the biomarkers represent only a minor portion of the TOC while the $\delta^{13}C$ ratios apply to the total organic carbon. In addition, as seen in the river data, there is a wider range of lignin phenol and plantwax *n*-alkane concentrations in the source material than there is of $\delta^{13}C$ ratios. This problem is particularly true for the lignin phenols, since there is the possibility that the lignin-rich vascular plant debris that is currently being deposited on the shelf could have been

deposited at this site in the past. The variability observed for the lignin phenol properties (e.g., S/V, C/V and Va/Vh) is greater than experimental error but less than the range seen in the river samples (Table 2). These results might indicate that this site did not receive a compositionally uniform input of terrestrial organic matter over the time frame represented by the sample set.

Although the general pattern of increasing terrestrial component with depth is seen by both approaches and with all tracers, the actual estimates of %TERR differ significantly at many depths in this core. The %TERR values derived from C/N_a data are most concurrent, although these estimates are suspect due to possible selective remineralization of organic nitrogen as inferred in the shelf sediments. Such selective loss of nitrogen would lead to an overestimate of the terrestrial TOC contribution to marine sediments. Despite this concern, %TERR estimated using C/N_a data are not the highest values. The %TERR values determined from $\delta^{13}C$ ratios are most divergent at low terrestrial TOC concentrations, such as the top of core, due to different estimates of the isotopic composition of the marine endmember. However, the marine endmember predicted from the plantwax *n*-alkane regression is based on few points and is significantly more positive than any isotopic TOC measurement in Washington coastal sediments. We suspect that with more data points, the marine isotopic endmembers determined from the lignin phenol and plantwax *n*-alkane regressions would coalesce to a value closer to the lignin phenol endmember. As discussed above, there is inherently more variability in the %TERR determined from the biomarker concentrations (approach 1) than by the bulk parameters (approach 2), due to the potential for the deposition of biomarker-enriched TOC, which is clearly present in the river sediments. These differences can only be evaluated through the use of multiple biomarker tracers.

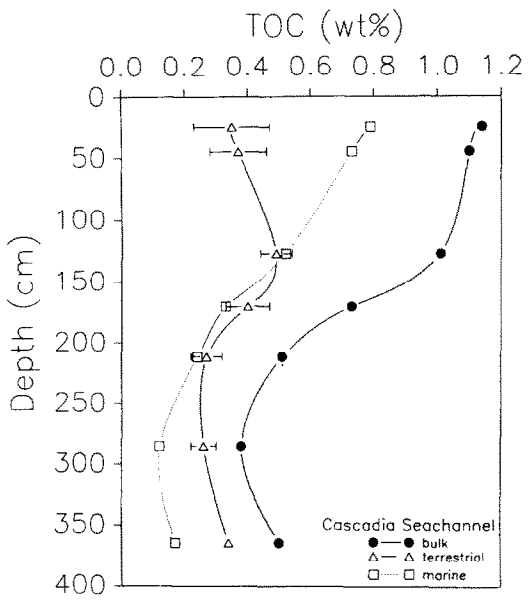

FIG. 6. Profiles for organic carbon (TOC and TOC apportioned into terrestrial and marine components) with depth in gravity core 6705-7 from Cascadia Seachannel. Terrestrial organic carbon concentrations (OC_{terr}) are calculated from estimates of %TERR (Table 5) and measured TOC (Table 4). Marine organic carbon concentrations (OC_{mar}) are calculated by difference using the expression, $TOC = OC_{terr} + OC_{mar}$.

%TERR results derived from the plantwax *n*-alkane and $\delta^{13}C$ data (Table 5) were averaged and used to apportion the TOC measured at each core depth into terrestrial (OC_{terr}) and marine (OC_{mar}) components (Fig. 6). The profile for OC_{terr} remains relatively uniform with depth (0.35 ± 0.07% by weight), while the depth profile for OC_{mar} mimics that of TOC. Various processes could act singly or in concert to explain the quantitative and compositional changes in TOC noted with depth in this core. Three key possibilities include (1) dilution of a fixed marine input with a variable input of land-derived mineral debris, (2) variable marine input (e.g., a change in phytoplankton productivity) with a fixed input of land-derived mineral debris, and (3) fixed input of both with preferential biodegradation of the marine relative to terrestrial component over time. A definitive oceanographic explanation is not yet possible given the poor stratigraphic constraint on this core and, furthermore, lies beyond the scope of our immediate work. However, this exercise demonstrates that organic geochemical information preserved in cores can be manipulated quantitatively to enrich an understanding of organic carbon burial in sediments accumulating along continental margins and elsewhere in the oceans (CALVERT and PEDERSEN, 1992, and references therein) and to refine existing models for the global carbon cycle (BERNER, 1989, and references therein).

CONCLUSIONS

The presence of terrestrial biomarkers in all sediments on the Washington margin and throughout the Cascadia Seachannel core clearly indicates the extent of the spatial and temporal distribution of riverine organic matter in the marine environment. The organic geochemical approaches employed in this research reveal the same general pattern of terrestrial TOC distribution, although the individual estimates of the terrestrial TOC content of marine sediments differ. These differences in the %TERR values are only apparent because we have been able to independently determine these estimates by the use of multiple organic geochemical tracers. A portion of these differences would be minimized with additional data, but there is an inherent variability in the biomarker concentration approach, which can only be realized and addressed through the use of multiple biomarkers.

The multiple tracer approach we used to constrain terrestrial contributions to TOC in sediments depositing along the Washington margin is potentially applicable to the study of other coastal marine environments. The calibrations needed to interpret quantitative biomarker information more than likely differ regionally because of geographic variations in the specific types of higher plant vegetation and degradative processes occurring within soils. Therefore, effort is required to calibrate empirically each region of interest. The usage of biomarker information to assess terrestrial contribution to TOC in marine sediments is still a relatively new field of research in need of refinement. Continued work along the lines we have pursued will allow more specific information about the carbon cycle to be extracted from the TOC record

preserved in marine sediments and thereby benefit paleoceanographic research. Sediments depositing along continental margins are particularly important to study because this region represents the major site of organic carbon burial in the ocean. Currently, interpretation of TOC records is complicated by our poor sense of the terrestrial and marine blend of source material preserved in sediments from this region and how this blend has changed through time.

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